

**A Method for Coating a Golf Ball With a Dry-On-Line Clear
Polyurethane Composition, and
Golf Balls Comprising Such a Coating**

Background of the Invention

(1) Field of the Invention

This invention relates generally to golf balls and golf ball coatings. More particularly, the present invention relates to golf balls having an improved polyurethane clear top coating that dries on-line without assistance of a plural machine, and to a method of coating a golf ball with a dry-on-line clear polyurethane. The coating system of this invention is particularly suitable for golf balls having a cover comprising an ionomer resin.

(2) Description of Related Art

A golf ball is generally classified into one of three types: a golf ball having a balata or urethane cover; a golf ball with a cover mainly composed of an ionomer resin; and an integrally molded type one-piece golf ball. All three of these golf balls are normally treated in order to impart a white appearance thereto, making the golf balls more visible against green grass.

Golf balls can also be classified according to the method of their assembly as either a "three-piece," a "two-piece" or a "one-piece" construction. The assembly of a golf ball generally involves molding a cover around a solid or wound core. Golf balls with wound cores are typically referred to as "three piece balls " because they consist of three basic components: (1) a solid or liquid-filled center; (2) rubber windings around the center; and (3) the cover.

Similarly, solid cores are referred to as having a "two piece" construction, since they consist solely of a solid core and a cover. A third type of ball, known as a "one-piece" ball is also known in the art. As the name suggests, one-piece balls are solid balls of homogeneous construction made by any conventional molding method suitable for the purpose.

The composition of the golf ball cover has proven to be a factor in overall golf ball performance. Historically, three-piece balls had covers made of balata. Balata is a natural resin, essentially made up of transpolyisoprene, and obtained from trees in South and Central America. Urethane covers are made from diisocyanates and polyols. Both a golf ball having a balata or urethane cover and an integrally molded type one-piece golf ball are coated with a paint containing a large amount of white pigment.

The majority of modern golf balls use a two-piece or three-piece construction with covers made of an ionomer resin such as Surlyn®, a product of E.I. DuPont de Nemours Company, Incorporated. An ionomeric resin is a polymer with covalent bonds between the elements of the chain, and ionic bonds between the chains. The Surlyn® covers are more cut-resistant than the balata covers.

In the case of a golf ball with a cover mainly composed of an ionomer resin, the ionomer resin itself is transparent, and the white pigment can also be formulated in the ionomer resin itself. Therefore, a white appearance can sometimes be obtained by only providing a clear layer without using the white paint.

There is a need for an improved clear polyurethane coating that will adhere well after weathering and that will resist abrasion. Good adhesion of the polyurethane coating after weathering and resistance of the coating to abrasion are particularly important for driving range balls, often referred to as "range balls." Because range balls are used in all kinds of weather, over and over again for many years, they need a tough and durable outer coating.

The durability and mechanical strength of an outer coating depend primarily on the chemical structure of the coating, the mechanical nature of the

coating, and the thickness of the coating. The chemical bonds in polyurethane are very strong. However the mechanical strength of the coating depends largely on the presence of an optimal length of urethane chain and an optimal density of crosslinkages. Two factors control chain length and density of crosslinkages. One such factor is the ratio of polyols and isocyanates used. The other factor is curing time. Generally, a longer curing time tends to provide better film mechanical properties of a urethane coating. Because mechanical strength is particularly important in range ball coatings, prior art polyurethane coatings used in the manufacture of range balls generally require approximately a 16 hour baking process in order to attain a durable urethane coating.

The durability of the urethane coating also depends on the thickness of the coating. Conventional practice is to either build up a thick coating of urethane through multiple spray applications of low-solid coatings or to apply a single layer of high solids coating. From a productivity standpoint, a single pass spray with high solids is more economical. However, a high-solid, single-pass spray presents technical difficulties. One disadvantage of a conventional single-pass spray process is that the material to be sprayed is very viscous and therefore difficult to spray. Another disadvantage of a conventional single-pass spray is that the thick layer produced dries slowly

and tends to sag, causing a non-uniform thickness of coat. The resultant ball is not uniformly spherical, and therefore exhibits poor flying performance.

Typical paints used to coat golf balls, including urethane golf balls, comprise two component polyurethane coatings, which have good impact resistance.

One of the problems associated with conventional two component polyurethane coatings is that they dry slowly. In order to speed up drying, a plural machine is usually used.

Because of the slow drying nature of conventional polyurethane coatings, the golf ball painting process requires many steps. In the conventional process for clear-coating a golf ball, the surface-prepared balls are first mechanically loaded onto a stamping machine that prints a logo or stamp on the balls. The balls are then continuously loaded onto spindles that carry the balls and travel along with a moving chain to pass by spray guns that apply a clear polyurethane top-coating to the balls. The chain then moves wet, painted balls through a heated oven to pre-cure the coating. When they reach the end of the oven, the painted balls are usually still not dry, and have to be manually unloaded from spindles on the moving chain onto holding racks. The holding racks with the balls are then placed into another heated oven to bake for another 16 hours or longer at 100 degrees Fahrenheit in order to completely cure the coating before further processing or handling. Due to the

slow-drying nature of a conventional clear coat polyurethane system, all these steps, especially the 16 hour baking process, are necessary.

The conventional painting process has many drawbacks. First, manually loading wet balls from spindles on a moving chain on to holding racks is very labor intensive and often results in damage or destruction of the surface of the balls. Due to human error, many well-painted balls are often accidentally dropped off from spindles on a moving chain line or off holding racks. The dropped balls are unusable and represent substantial annual capital loss.

Secondly, there is a substantial labor cost to unload cured balls from the racks into collecting hoppers for further processing. Thirdly, oven baking for 16 hours is time-consuming and consumes a substantial amount of energy. The ovens are large and require a large amount of floor space, which is also costly. The number of steps reduces productivity substantially.

In addition, an inevitable, substantial problem is that unloading wet balls off spindles onto loading racks often leaves balls with scratches or pin marks because the balls with wet paint have to be touched by another device. These scratches or marks are major causes of quality control rejection for surface defects.

An even greater problem is that the heating of the balls for the required drying time in the ovens deteriorates the rubber thread wound inside urethane balls. The performance of urethane balls depends substantially on the elasticity of the rubber thread wound inside the balls. The rubber thread windings have been analogized to an "engine" of a wound ball. The deterioration by heat is due to the associated loss of elasticity of rubber thread wound inside wound balls, and the resulting loss of performance.

Fast drying of the applied coating and long "pot life" of the urethane coating materials are both properties desired by painters working with urethane coatings. However, the fast drying and long pot life are properties that contradict each other. That is, the faster drying a formula is, generally the shorter the pot life is. To compromise, common practice in the industry is to use a so-called "plural component machine" or simply "plural machine" which mixes component A with component B containing a catalyst just before the coating reaches the spray gun. This approach satisfies the painter's need to have a long pot life because components A and B are separated until the coating material reaches the spray gun. However, the plural machine is very expensive and one machine can serve only one paint line. If a shop has many paint lines, the capital investment is substantial.

For the foregoing reasons, there is a need for an improved clear polyurethane coating for golf balls which can be applied in a single spray, and which will dry quickly on-line without requiring oven-baking and for a method for coating a golf ball with the improved, fast-drying, single spray polyurethane.

Summary of the Invention

The present invention satisfies these needs with a clear polyurethane coating for golf balls that dries on-line in approximately 10 minutes without assistance of any plural machine, a coating that can be applied in a single spray, that dries without sagging and that is tough and durable, and with a method for coating golf balls that comprises using the coating composition and the coating system of the invention.

Accordingly, the main object of the invention is to provide an improved clear polyurethane coating for golf balls that dries quickly on-line, and a method for applying the improved coating.

A further object of the invention is to provide a fast-drying, clear polyurethane coating that can be applied in a single spray, is uniform in thickness, and imparts a shiny, smooth surface to golf balls.

Another object of the invention is to provide a fast-drying, clear polyurethane coating and a method for applying the coating that produce golf balls that are free of surface defects caused by wet balls being touched by another device.

Another object of the invention is to provide a fast-drying, clear polyurethane coating that has good impact resistance and that is suitable to paint golf balls having ionomeric resin covers.

Another object of the invention is to provide a simple formulation using a catalyst system that causes the coating to dry in a period of approximately 10 minutes and yet has good pot life and a constant viscosity over the course of that pot life.

Yet a further object of the invention is to eliminate the need for manually loading and unloading wet balls from spindles on a moving chain onto holding racks. By eliminating the need for manual loading and unloading, labor cost is reduced and the number of balls dropped and damaged during handling is substantially reduced.

Another object of the invention is to eliminate the need for a second oven-baking of wet-coated balls before further handling or processing. By eliminating the need for the second oven-baking, which in the conventional method is carried out at a high temperature for 16 hours, energy and floor space costs are significantly reduced and loss of performance of balls due to heat deterioration of interior rubber windings is eliminated.

Another object of the invention is to provide an improved coating system and method for coating golf balls that allow the coated balls to be collected into containers directly from the painting line to be further processed .

The foregoing and other objects of the invention have been attained by providing a clear polyurethane coating for golf balls and a coating system that uses a drying accelerator which is part of the present invention. The drying accelerator substantially shortens the drying time of the clear polyurethane coating. In addition, the combination of catalysts used in the drying accelerator results in a viscosity that is more constant than that provided by a single catalyst used in conventional systems. In conventional single catalyst systems there is a need to continually adjust the focus and air pressure of the spray guns due to rapidly changing viscosity.

The accelerator is comprised of two metal catalysts which have a synergistic effect on the drying of the polyurethane coating. It is critical that both catalysts are used together, because if only one of the catalysts is used, the effect on drying time is substantially less. One of the catalysts comprises a chelated zirconium complex, available commercially as K-Kat 4205. The other catalyst, which works in synergism with the zirconium catalyst is dibutyl tin di-laurate (DBTDL), commercially available as Metacure T-12. This combination imparts novel fast drying characteristics to the coating so that it dries on-line in a period of 10 minutes at temperatures of 170 to 180°F, yet has reasonable pot life. The pot life is over 2 hours. This desirable balance between fast drying characteristics

and adequate pot life satisfies a long felt need in the industry, and would not be obtained by using either of the catalysts separately.

The coating system also uses a surfactant to improve flow properties of the coating material to be sprayed and to impart a shiny, smooth surface to the coated balls. This is important in golf ball coatings because of the dimples on the surface of golf balls. If the coating material to be sprayed on the balls has poor flow characteristics, the coating material will flood the dimples. The result will be uneven coating of the dimples. Because the dimples control the overall flying performance of the balls, the uneven coating will adversely affect the flying performance of the balls. In this invention, a fluorosurfactant containing fluoroaliphatic polymeric esters in ethyl acetate is used. The fluorosurfactant is commercially available as Fluorad-431. Other surfactants would also work. Fluorad-431 is preferred.

The paint system in this invention comprises a polyurethane coating mixture, a two-component drying accelerator, and a surfactant. The unique drying accelerator and the surfactant were briefly described above. The polyurethane coating system is a conventional system comprising polyols, isocyanates, and solvents. The coating system of this invention, including the unique drying accelerator and the fluorosurfactant, provides a coating with good impact resistance, good adhesion, flexibility, abrasion resistance, and toughness. These are necessary characteristics of a coating system for golf balls, especially for range balls. The system would be extremely slow-drying but for the unique two-component catalyst of the invention.

Thus the dry-on-line clear polyurethane coating for golf balls and the golf ball coating method of the present invention provide a substantially faster manufacturing process with much less heat exposure and a much greater percentage of golf balls produced without surface defects than in conventional golf ball coating systems. The result is a substantial capital savings for the manufacturer and better performing balls due to less heat exposure in the coating process than in conventional systems. The painted golf balls produced in accordance with this invention have significantly improved flying accuracy.

Brief Description of the Drawings.

Figure 1 depicts a side elevation view of an embodiment of a schematic procedure for spraying golf balls with a Dry-On-Line Clear Polyurethane Composition.

Description of the Preferred Embodiments

At the outset the invention is described in its broadest overall aspects with a more detailed description following. The fast-drying property of the paint system in this invention revolutionizes the whole painting process into so-called dry-on-line. The present invention is a clear polyurethane coating system suitable for golf balls that dries on-line in a period of approximately 10 minutes under elevated temperature. Thus the painted balls can be dried on-line and mechanically transferred for further processing.

The method of this invention is performed as follows: Golf balls having a pigment such as white, yellow, or any other color mixed into the golf ball cover are provided. For proper coating adhesion, the surfaces of the balls are prepared by conventional methods, including removal of dirt and grease from the surface. In addition, the surfaces are "roughened" to increase surface area. The surface-prepared balls are mechanically loaded onto a stamping machine by which logos or stamps are printed.

As shown in Fig. 1, the golf balls 10a, 10b, 10c are loaded onto spindles 12a, 12b, 12c, on a chain 14. The chain is moved by a drive system 16. The chain moves and carries the balls past a first set of spray guns 5a, 5b, that apply one coat of a conventional primer paint to the balls. The primer paint comprises aziridine and an acrylic-urethane emulsion in water and other solvents. The chain moves the balls into a first oven 6 where they are heated for about one to two minutes. The clear coating is applied immediately after the balls exit the first oven. To apply the clear coating, the balls are carried by the chain past a second set of spray guns 18a, 18b. The balls 10a, 10b, 10c are sprayed with the clear polyurethane coating composition of this invention, and are moved along with the chain 14 into a heated oven 20. The chain travels in the oven 20 for a period of 10 to 15 minutes. When the balls exit the oven after the 10 to 15 minute period, they are sufficiently dry to allow them to be mechanically knocked off directly from spindles into collecting hoppers for further processing.

Thus, the coating system of this invention eliminates the steps of manually loading wet, clear-coated balls; it eliminates 16 hours of drying time for the clear coat in a second

oven; the need for a second oven; and manually unloading cured balls into collecting hoppers. Furthermore, the dry-on-line process reduces quality rejection due to reduction in the number of balls with surface defects. The dry-on-line process also maintains wound ball performance as designed because the process requires significantly less exposure to high heat than conventional systems. Flight performance is also improved because of even-coating of the dimples resulting from the single-spray, high solid, low viscosity, fast-drying nature of the coating system of this invention.

The coating system in this invention comprises a polyurethane clear coating mixture, a drying accelerator and a surfactant. The coating mixture that has a component of polyester polyols, of isocyanates, and of solvents is supplied by Technical Coating Laboratory, Inc., hereinafter referred to as "TCL," in Avon, Connecticut. The polyurethane clear coating mixture is a clear base, commercially available as TCL 6249, comprising polyester polyols.

The ingredients of TCL 6249 include the following:

<u>Component</u>	<u>Weight percent (approximate)</u>
Propylene glycol monomethyl ether acetate	2
Xylene	1
N-butyl acetate	14
Ethyl acetate	16
Toluene	26
Cyclohexanone	< 0.5%
Mineral spirits	< 0.5%
Ethyl benzene	< 0.5%
Non-volatiles	40.9

The clear base, TCL 6249, is mixed with the activator, commercially available as TCL 6263, comprising a blend of aliphatic and aromatic isocyanates.

The ingredients of TCL 6263 include the following:

<u>Component</u>	<u>Weight percent (approximate)</u>
Hexamethylene diisocyanate	1
Xylene	11
N-butyl acetate	17
Toluene	8
Non-volatiles	64.1

The fluorosurfactant used in this invention, as previously stated, contains fluoroaliphatic polymeric esters in ethyl acetate, and is commercially available as Fluorad-431.

The ingredients of Fluorad-431 include the following:

<u>Component</u>	<u>Weight percent (approximate)</u>
Potassium fluoroalkyl carboxylate(C8)	40.0 to 44.0
Water	32.0
2-Butoxyethanol	14.0
Ethyl alcohol	4.0
Potassium fluoroalkyl carboxylate(C6)	1.0 to 5.0
Potassium fluoroalkyl carboxylate(C4)	1.0 to 5.0
Potassium fluoroalkyl carboxylate(C7)	1.0 to 3.0
Potassium fluoroalkyl carboxylate(C5)	0.1 to 1.0

It is known that reactions of polyols with isocyanates forming polyurethane linkage follow a nucleophilic reaction mechanism. The reaction starts with a lone pair of

electrons of oxygen in a hydroxy group of polyols first attacking a carbonyl carbon of an isocyanate group. The reaction speed will be greatly increased if any dissociation of hydrogen in a hydroxy group of polyols occurs since it empowers nucleophilic attack of oxygen due to increase of its electron density.

It is known that chelated zirconium such as K-Kat 4205 catalyzes the curing of 2-component urethane coatings. It is also known that dibutyl tin dilaurate (DBTDL) catalyzes the curing of polyurethane. However, the invention is directed to the combining of the two catalysts, ~~chelated zirconium and~~ DBTDL, which the inventors discovered has a dramatic, synergistic effect on both curing time and the uniformity of coating and on the flying accuracy of a golf ball coated with the coating system of the invention.

As described previously, one of the catalysts comprises a chelated zirconium complex, available commercially from King Industry as K-Kat 4205. The amount of K-Kat 4205 used in the present invention is 1.2% on resin solid. If it were the only catalyst present in the coating mixture, the Zirconium complex in K-Kat 4205 is believed to act as a Lewis acid interacting with the hydrogen in a hydroxy group of a polyol. Thus, the nucleophilic attacking power of the oxygen in a hydroxy group is greatly increased. As a result of the foregoing mechanism, the drying of the polyurethane coating speeds up.

In order to provide a coating system which dries quickly on-line, it is critical that the polyurethane coating mixture includes a drying accelerator comprising two catalysts, a

chelated zirconium complex and dibutyl tin dilaurate, which act in synergism with one another to greatly speed drying time. The mechanism for the synergism of the two catalysts is unknown.

The following examples are illustrative for mixing procedure and application conditions of the coating system of the invention. The examples are provided for illustration but are not to be considered as limiting.

Example 1

Preparation of Catalyst Solution

For optimal results, the catalyst solution should be freshly prepared. Into a container, add 10.0 grams of K-Kat 4205 and 0.3 grams Metacure T-12. Stir until the two catalysts are well mixed, forming "Mixture 1."

To prepare the catalyst solution, into a second container, add 4.7 grams of the Mixture 1. Then add the following into the second container: 10.0 grams of FC-431, 32.0 grams of parachlorobenzotrifluoride (PCBTF), and 32.0 grams of acetone. PCBTF is commercially available as Oxsol-100, supplied by Oxychem. Mix the ingredients present in the second container well. The catalyst solution in the second container is ready to use as soon as it is well-mixed. The total amount of the two component catalyst system is 78.7 grams. The catalyst solution should be kept covered as long as possible to minimize loss of solvent by evaporation.

Example 2

Preparation of Urethane Clear Coat

<u>Ingredients</u>	<u>Code</u>	<u>Solid %w/w</u>	<u>Amount</u>
Clear base	TCL 6249	40.90	550.0 grams
Activator	TCL 6263	64.10	290.0 grams
Catalyst solution		0.00	<u>78.7 grams</u>
Total			918.7 grams

Example 2 illustrates the preparation of a clear coating system which is used to coat golf balls, particularly range balls. The ingredients in the above table are mixed according to the following procedure.

At room temperature, the following materials are added to a container: 550.0 grams of clear base TCL 6249, 290.0 grams of activator TCL 6263 and 78.7 grams of catalyst solution from Example 1. The container is put on a shaker to shake for 5 minutes. The clear coating mixture is ready to spray golf balls.

In the above table for Example 2, the critical ratio of coating components is 550.0 grams of TCL 6249 to 290.0 grams of TCL 6263. The preferred range is plus or minus 10% from the critical ratio. The catalyst will work with any ratio of polyols and isocyanates.

Example 3

Method of Applying a Clear Urethane Coating Mixture

Provide a freshly-prepared catalyst mixture prepared according to Example 1, and a urethane clear coat mixture prepared according to Example 2. Provide golf balls having

a pigment such as white, yellow, or any other color mixed into the golf ball cover.

Prepare the surface of the golf balls by removing dirt and grease. Roughen the surface of the golf balls. Mechanically load the surface-prepared balls onto a stamping machine by which logos or stamps are printed. Apply one coat of a conventional primer paint to the golf balls. This is done on-line, prior to the application of clear coat. As shown in Fig. 1, load the golf balls 10a, 10b, 10c onto spindles 12a, 12b, 12c on a chain 14. Connect the chain to a drive system 16 which moves the chain and carries the balls past a first set of spray guns 5a, 5b that apply one coat of a conventional primer paint to the balls.

Move the balls on-line into a first oven 6 and allow them to be heated for about one to two minutes. When the balls exit the oven continue to move them past a second set of spray guns 18a, 18b to be sprayed with clear coating while the balls are still warm.

Adjust the spray guns and chain speed to control the total weight of wet clear paint on a ball to between 200.0 and 210.0 mg. Adjust the chain speed of the painting line to 23.0 ft./min. (equivalent to painting 130 balls per minute).

The chain 14 moves and carries the balls 10a, 10b, 10c past spray guns 18a, 18b. The balls 10a, 10b, 10c are sprayed with the clear polyurethane coating composition of this invention, and are moved along with the chain 14 into a heated oven 20. The oven temperature is at 180° Fahrenheit. Allow the chain to travel in the oven 20 for a period of 10 to 15 minutes. When the balls exit the oven after the 10 to 15 minute period, they are sufficiently dry to allow them to be mechanically knocked off directly from spindles into collecting hoppers for further processing.

In this example, only one coat of polyurethane coating is applied. The polyurethane coating is "high solids," containing more than 40% solids, but is applied in a single-pass spray. This is unlike conventional single-pass spray coating systems, in which the high solid spray is too viscous for even coating. The viscosity of the high solid spray of the present invention is sufficiently low to make spraying easy. The clear coating is uniformly thick and the coated ball exhibits excellent flying characteristics.

Contrary to the "plural component machine" approach, the invention provides a balance between drying speed and pot life of urethane coatings. The composition of the invention dries in a period of 10 minutes at a temperature of about 180° Fahrenheit, yet still has a pot life of over 2 hours. This balance not only meets a fast drying requirement, but also offers reasonable pot life to painters. Coating properties of the invention are excellent.

This polyurethane coating has good adhesion, flexibility, abrasion resistance and toughness. However, without the critical combination of catalysts to which the present invention is directed, the coating would dry slowly and require all the steps of conventional systems described previously.

While the present invention has been described in connection with preferred embodiments thereof, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the true spirit and scope of the present invention. Accordingly, it is intended by the

appended claims to cover all such changes and modifications as come within the true spirit and scope of the invention.

11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000
1001
1002
1003
1004
1005
1006
1007
1008
1009
1010
1011
1012
1013
1014
1015
1016
1017
1018
1019
1020
1021
1022
1023
1024
1025
1026
1027
1028
1029
1030
1031
1032
1033
1034
1035
1036
1037
1038
1039
1040
1041
1042
1043
1044
1045
1046
1047
1048
1049
1050
1051
1052
1053
1054
1055
1056
1057
1058
1059
1060
1061
1062
1063
1064
1065
1066
1067
1068
1069
1070
1071
1072
1073
1074
1075
1076
1077
1078
1079
1080
1081
1082
1083
1084
1085
1086
1087
1088
1089
1090
1091
1092
1093
1094
1095
1096
1097
1098
1099
1100
1101
1102
1103
1104
1105
1106
1107
1108
1109
1110
1111
1112
1113
1114
1115
1116
1117
1118
1119
1120
1121
1122
1123
1124
1125
1126
1127
1128
1129
1130
1131
1132
1133
1134
1135
1136
1137
1138
1139
1140
1141
1142
1143
1144
1145
1146
1147
1148
1149
1150
1151
1152
1153
1154
1155
1156
1157
1158
1159
1160
1161
1162
1163
1164
1165
1166
1167
1168
1169
1170
1171
1172
1173
1174
1175
1176
1177
1178
1179
1180
1181
1182
1183
1184
1185
1186
1187
1188
1189
1190
1191
1192
1193
1194
1195
1196
1197
1198
1199
1200
1201
1202
1203
1204
1205
1206
1207
1208
1209
1210
1211
1212
1213
1214
1215
1216
1217
1218
1219
1220
1221
1222
1223
1224
1225
1226
1227
1228
1229
1230
1231
1232
1233
1234
1235
1236
1237
1238
1239
1240
1241
1242
1243
1244
1245
1246
1247
1248
1249
1250
1251
1252
1253
1254
1255
1256
1257
1258
1259
1260
1261
1262
1263
1264
1265
1266
1267
1268
1269
1270
1271
1272
1273
1274
1275
1276
1277
1278
1279
1280
1281
1282
1283
1284
1285
1286
1287
1288
1289
1290
1291
1292
1293
1294
1295
1296
1297
1298
1299
1300
1301
1302
1303
1304
1305
1306
1307
1308
1309
1310
1311
1312
1313
1314
1315
1316
1317
1318
1319
1320
1321
1322
1323
1324
1325
1326
1327
1328
1329
1330
1331
1332
1333
1334
1335
1336
1337
1338
1339
1340
1341
1342
1343
1344
1345
1346
1347
1348
1349
1350
1351
1352
1353
1354
1355
1356
1357
1358
1359
1360
1361
1362
1363
1364
1365
1366
1367
1368
1369
1370
1371
1372
1373
1374
1375
1376
1377
1378
1379
1380
1381
1382
1383
1384
1385
1386
1387
1388
1389
1390
1391
1392
1393
1394
1395
1396
1397
1398
1399
1400
1401
1402
1403
1404
1405
1406
1407
1408
1409
1410
1411
1412
1413
1414
1415
1416
1417
1418
1419
1420
1421
1422
1423
1424
1425
1426
1427
1428
1429
1430
1431
1432
1433
1434
1435
1436
1437
1438
1439
1440
1441
1442
1443
1444
1445
1446
1447
1448
1449
1450
1451
1452
1453
1454
1455
1456
1457
1458
1459
1460
1461
1462
1463
1464
1465
1466
1467
1468
1469
1470
1471
1472
1473
1474
1475
1476
1477
1478
1479
1480
1481
1482
1483
1484
1485
1486
1487
1488
1489
1490
1491
1492
1493
1494
1495
1496
1497
1498
1499
1500
1501
1502
1503
1504
1505
1506
1507
1508
1509
1510
1511
1512
1513
1514
1515
1516
1517
1518
1519
1520
1521
1522
1523
1524
1525
1526
1527
1528
1529
1530
1531
1532
1533
1534
1535
1536
1537
1538
1539
1540
1541
1542
1543
1544
1545
1546
1547
1548
1549
1550
1551
1552
1553
1554
1555
1556
1557
1558
1559
1560
1561
1562
1563
1564
1565
1566
1567
1568
1569
1570
1571
1572
1573
1574
1575
1576
1577
1578
1579
1580
1581
1582
1583
1584
1585
1586
1587
1588
1589
1590
1591
1592
1593
1594
1595
1596
1597
1598
1599
1600
1601
1602
1603
1604
1605
1606
1607
1608
1609
1610
1611
1612
1613
1614
1615
1616
1617
1618
1619
1620
1621
1622
1623
1624
1625
1626
1627
1628
1629
1630
1631
1632
1633
1634
1635
1636
1637
1638
1639
1640
1641
1642
1643
1644
1645
1646
1647
1648
1649
1650
1651
1652
1653
1654
1655
1656
1657
1658
1659
1660
1661
1662
1663
1664
1665
1666
1667
1668
1669
1670
1671
1672
1673
1674
1675
1676
1677
1678
1679
1680
1681
1682
1683
1684
1685
1686
1687
1688
1689
1690
1691
1692
1693
1694
1695
1696
1697
1698
1699
1700
1701
1702
1703
1704
1705
1706
1707
1708
1709
1710
1711
1712
1713
1714
1715
1716
1717
1718
1719
1720
1721
1722
1723
1724
1725
1726
1727
1728
1729
1730
1731
1732
1733
1734
1735
1736
1737
1738
1739
1740
1741
1742
1743
1744
1745
1746
1747
1748
1749
1750
1751
1752
1753
1754
1755
1756
1757
1758
1759
1760
1761
1762
1763
1764
1765
1766
1767
1768
1769
1770
1771
1772
1773
1774
1775
1776
1777
1778
1779
1780
1781
1782
1783
1784
1785
1786
1787
1788
1789
1790
1791
1792
1793
1794
1795
1796
1797
1798
1799
1800
1801
1802
1803
1804
1805
1806
1807
1808
1809
1810
1811
1812
1813
1814
1815
1816
1817
1818
1819
1820
1821
1822
1823
1824
1825
1826
1827
1828
1829
1830
1831
1832
1833
1834
1835
1836
1837
1838
1839
1840
1841
1842
1843
1844
1845
1846
1847
1848
1849
1850
1851
1852
1853
1854
1855
1856
1857
1858
1859
1860
1861
1862
1863
1864
1865
1866
1867
1868
1869
1870
1871
1872
1873
1874
1875
1876
1877
1878
1879
1880
1881
1882
1883
1884
1885
1886
1887
1888
1889
1890
1891
1892
1893
1894
1895
1896
1897
1898
1899
1900
1901
1902
1903
1904
1905
1906
1907
1908
1909
1910
1911
1912
1913
1914
1915
1916
1917
1918
1919
1920
1921
1922
1923
1924
1925
1926
1927
1928
1929
1930
1931
1932
1933
1934
1935
1936
1937
1938
1939
1940
1941
1942
1943
1944
1945
1946
1947
1948
1949
1950
1951
1952
1953
1954
1955
1956
1957
1958
1959
1960
1961
1962
1963
1964
1965
1966
1967
1968
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
1984
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
2024
2025
2026
2027
2028
2029
2030
2031
2032
2033
2034
2035
2036
2037
2038
2039
2040
2041
2042
2043
2044
2045
2046
2047
2048
2049
2050
2051
2052
2053
2054
2055
2056
2057
2058
2059
2060
2061
2062
2063
2064
2065
2066
2067
2068
2069
2070
2071
2072
2073
2074
2075
2076
2077
2078
2079
2080
2081
2082
2083
2084
2085
2086
2087
2088
2089
2090
2091
2092
2093
2094
2095
2096
2097
2098
2099
2100
2101
2102
2103
2104
2105
2106
2107
2108
2109
2110
2111
2112
2113
2114
2115
2116
2117
2118
2119
2120
2121
2122
2123
2124
2125
2126
2127
2128
2129
2130
2131
2132
2133
2134
2135
2136
2137
2138
2139
2140
2141
2142
2143
2144
2145
2146
2147
2148
2149
2150
2151
2152
2153
2154
2155
2156
2157
2158
2159
2160
2161
2162
2163
2164
2165
2166
2167
2168
2169
2170
2171
2172
2173
2174
2175
2176
2177
2178
2179
2180
2181
2182
2183
2184
2185
2186
2187
2188
2189
2190
2191
2192
2193
2194
2195
2196
2197
2198
2199
2200
2201
2202
2203
2204
2205
2206
2207
2208
2209
2210
2211
2212
2213
2214
2215
2216
2217
2218
2219
2220
2221
2222
2223
2224
2225
2226
2227
2228
2229
2230
2231
2232
2233
2234
2235
2236
2237
2238
2239
2240
224